Final Report for AOARD Grant 104144

"Novel routes to tune thermal conductivities and thermoelectric properties of materials"

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Abstract:
The goal of this project is to find novel routes to tune thermal conductivities and thermoelectric properties of materials mainly composed of relatively abundant light elements like boron, carbon, nitrogen, silicon, sulfur, oxygen, etc. We mainly focus on control of the atomic network structure and symmetry in crystal structure of inorganic materials to lead to dramatic effects in the properties. I list the main results.
One particularly studied system in the work was the recently discovered potential n-type counterpart ($YB2_2C_2N$ as a representative) to p-type boron carbide, which is one of the few thermoelectric materials with a history of commercialization.
As a byproduct of attempting further control of the network structure by utilizing atomic bridging sites, we have discovered an anomalous vanadium doping effect in $YB_{22}C_2N$ that increased the electrical conductivity by 50,000% while simultaneously increasing the Seebeck coefficient by 220%. Selective transition metal doping was also clearly demonstrated to modify the crystal structure of a borosilicide, leading to significant increase of the thermoelectric power factor and change of sign in the Seeebeck coefficient. Such demonstration of the possibility to modify the crystal structures can expand the possibilities of borides as functional compounds.
A series of indium-free novel TCO compounds with novel crystal structures, has revealed exceptionally low thermal conductivity through its homologous nature and mixing of the cation sites, and exhibited thermoelectric properties indicated to be better than the extensively studied IZO, as an n-type oxide. Furthermore, as an example of material design utilizing particular crystal structures, a unified description for crystal structures of another new homologous series in the gallium zinc oxides was formulated.
Silicon or germanium based cage compounds with low thermal conductivity were also found to reveal enhanced properties through small substitution of the network atoms.
A potential replacement material to boron carbide, having related crystal structure, boron sulfide B_6S_{1-x}, with S-S atoms bridging the boron clusters, was revealed to exhibit similar large thermopower at high temperatures, with much lower processing temperatures than boron carbide.
To summarize, by focusing on control and design of crystal structures, novel promising thermoelectric materials with low thermal conductivity were discovered or powerful methods for modification were demonstrated in the borides, silicides and oxides.

Introduction:

The goal of this project is to find novel routes to tune thermal conductivities and thermoelectric (TE) properties of materials, which will pave the way for the first wide scale application of thermoelectric power generation from waste heat. Approximately two thirds of all primary energy (fossil fuels, etc.) being consumed in the world, sadly turns out to be unutilized, with much of the waste being in the form of heat. The useful and direct energy conversion of waste heat to electricity is a large incentive to find viable thermoelectric materials. Traditionally high performance TE materials have tended to contain rather undesirable elements like Pb, Te, Bi, Ag, etc. which are obstacles to their wide-spread usage. A large goal is to find ways to highly functionalize common, relatively light elements like B, Si,

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14. ABSTRACT

The goal of this project was to find novel routes to tune thermal conductivities and thermoelectric properties of materials mainly composed of relatively abundant light elements like boron, carbon, nitrogen, silicon, sulfur, oxygen, etc. Focus was on the control of the atomic network structure and symmetry in crystal structure of inorganic materials to lead to dramatic effects in the properties. One particularly studied system in the work was the recently discovered potential n-type counterpart (YB22C2N as a representative) to p-type boron carbide, which is one of the few thermoelectric materials with a history of commercialization. As a byproduct of attempting further control of the network structure by utilizing atomic bridging sites, we have discovered an anomalous vanadium doping effect in YB22C2N that increased the electrical conductivity by 50,000% while simultaneously increasing the Seebeck coefficient by 220%. Selective transition metal doping was also clearly demonstrated to modify the crystal structure of a borosilicide, leading to significant increase of the thermoelectric power factor and change of sign in the Seebeck coefficient. Such demonstration of the possibility to modify the crystal structures can expand the possibilities of borides as functional compounds. A series of indium-free novel TCO compounds with novel crystal structures, has revealed exceptionally low thermal conductivity through its homologous nature and mixing of the cation sites, and exhibited thermoelectric properties indicated to be better than the extensively studied IZO, as an n-type oxide. Furthermore, as an example of material design utilizing particular crystal structures, a unified description for crystal structures of another new homologous series in the gallium zinc Silicon or germanium based cage compounds with low thermal conductivity were also found to reveal enhanced properties through small substitution of the network atoms. A potential replacement material to boron carbide, having related crystal structure, boron sulfide B6S1-x, with S-S atoms bridging the boron clusters, was revealed to exhibit similar large thermopower at high temperatures, with much lower processing temperatures than boron carbide. To summarize, by focusing on control and design of crystal structures, novel promising thermoelectric materials with low thermal conductivity were discovered or powerful methods for modification were demonstrated in the borides, silicides and oxides.

15. SUBJECT TERMS

thermal management materials , thermal transport

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Al, etc. which can have a huge impact on the sustainability and wide-spread usage of functional materials.

The XIII~XV group elements (C, B, Si, Al, Sn, etc.) have been known to form covalent compounds wi th particular network-like structures, i.e. clusters, 2D atomic nets, cage-like structures in which the str uctural order plays a large role in the physical properties. We are mainly interested i n the non-carbon materials which have not been as well studied as their carbon counterparts. We fo cus on the network structure as a route to endow these relatively light element compounds wi th functionalities, and as seeds, we have found that it appears possible to have a degree of c ontrol over the atomic network structure which has led to dramatic effects in the TE properties.

Namely, we have recently discovered that small amounts of third elements like carbon, nitrogen, and s ilicon can sometimes function as bridging sites, and result in the formation of novel and varied boron cluster structures. As a result, a series of homologous compounds; $YB_{17}CN$, $YB_{22}C_2N$, and $YB_{28.5}C_4$, was recently discovered to be the long awaited n-type counterpart to boron carbide.

In this work, we investigate various doping experiments in an attempt to find routes to furthe r modify the network structure and enhance physical properties. Namely, we mainly focus on control of the atomic network structure and symmetry in inorganic materials to lead to dramat ic effects in the thermal conductivities and thermoelectric properties

Experiment: High temperature synthesis methods were employed to synthesize and develop the thermoelectric borides, silicides, and oxides studied in this project.

Results and Discussion:

The results described in the abstract are well described in detail in the refereed publications attached.

We add a little more detail on some works which are still in press.

Boron sulfides: B_6S_{1-x}

Boron carbide ($B_{4.3}C$ - $B_{\sim 11}C$) has been extensively studied due to its attractive thermoelectric properties. We focused on boron-rich compounds with sulfur instead of carbon, of which there has only been an early report on existence of $B_{12}S$-$B_{12}S_{1.3}$ phase structurally belonging to the *α-rh* B group.

B_6S_{1-x} samples ($0.37<x\leq 0.40$) have been prepared from weighed mixtures of starting components which were well mixed with gallium and compacted into pellets applying ~30 MPa of pressure. An excess of sulfur (about 10 wt. %) was used to compensate the losses due to evaporation. The reaction process was performed in a BN crucible under a flow of Ar at about 1473 -1573 K for 4 hours; afterwards the setup was cooled down in 1 hour to room temperature. X-ray powder diffraction structural studies showed that similar to B_6O and B_6P structures, the boron atoms form a framework of B_{12} icosahedra which are bonded to each other and to S-S units are located in the interstices extended along the *c* axis of the rhombohedral unit cell (Fig. 1). The S-S distance (2.386 Å) is larger than the typical value of 2.08 Å for the S-S tetrahedral bond length, indicating weak bonding interaction between sulfur atoms. Rietveld refinements indicated the existence of a small homogeneity range revealing the population level of sulfur atom site around 60% - 63%. All samples possess *p*-type conductivity, and the electrical resistivity decreases with temperature in agreement with the properties of semiconductor material. The thermopower of B_6S_{1-x} exhibited large values similar to boron carbide (Fig. 2). While the samples have quite low density and therefore, low power factor, if a densification process can be developed, since sulphur is also quite abundant, B_6S_{1-x} may be an alternate to boron carbide, with a much lower processing temperature.

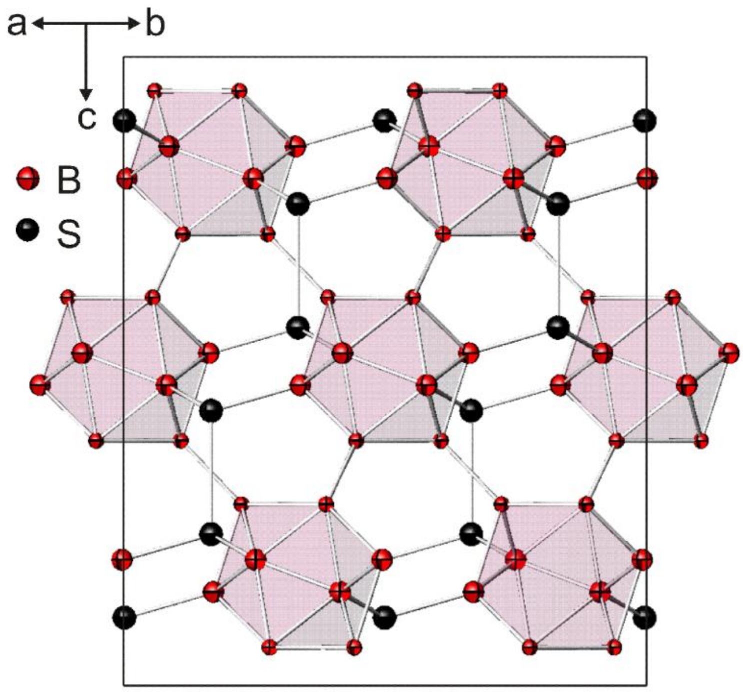

Fig. 1: View of crystal structure of B_6S_{1-x}.

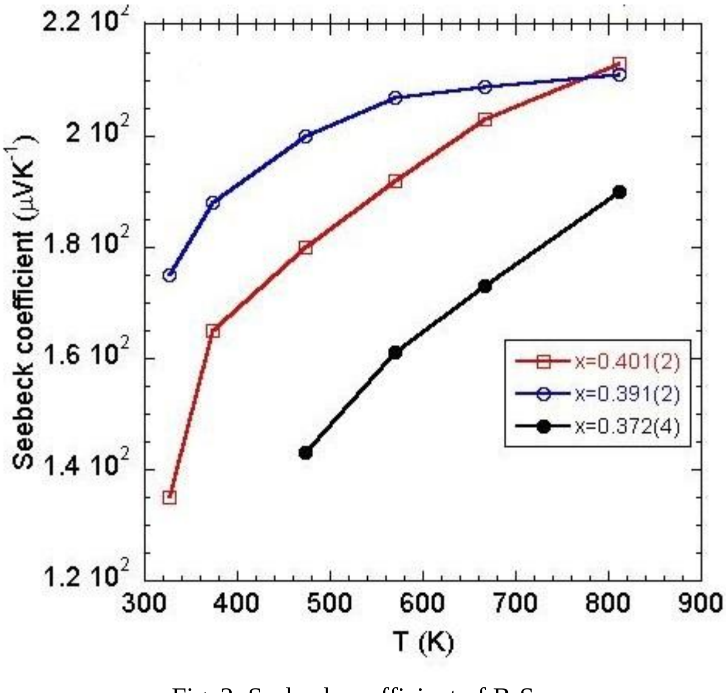

Fig. 2: Seebeck coefficient of B_6S_{1-x}.

Anomalous vanadium doping effect

We have been investigating transition metal doping as a way to modify the network structures and enhance physical properties. Several notable results have been obtained as described in the attached refereed paers. Vanadium boride seeded $YB_{22}C_2N$ were synthesized and the thermoelectric properties investigated and analyzed. $YB_{22}C_2N$ is representative of the series of rare earth borocarbonitrides which is the potential long awaited n-type counterpart to p-type boron carbide. VB_2 seeded samples of

$YB_{22}C_2N$ were prepared using VB_2 directly as an initial additive and V_2O_3 which also results in formation of vanadium diboride in the final product. The resistivity and Seebeck coefficient of samples were measured in the temperature range of 323 K to 1073 K. A dramatic effect of thermal treatment on both resistivity and Seebeck coefficient of VB_2 seeded samples was observed. Analyses of the influence of VB_2 amount in the samples and thermal treatment on thermoelectric properties of $YB_{22}C_2N$ were carried out, and from a theoretical analysis it is indicated that there is partial diffusion of the transition metal dopant into the boron cluster lattice. VB_2 was revealed to be a powerful additive to improve the thermoelectric properties of $YB_{22}C_2N$. An enhancement of more than 220% of the maximum absolute value of the Seebeck coefficient was obtained while the resistivity was also simultaneously reduced by 50,000%.

This is a striking effect and further investigation of transition metal doping into metal borides should be investigated as a follow on work.

Doping into the network framework:

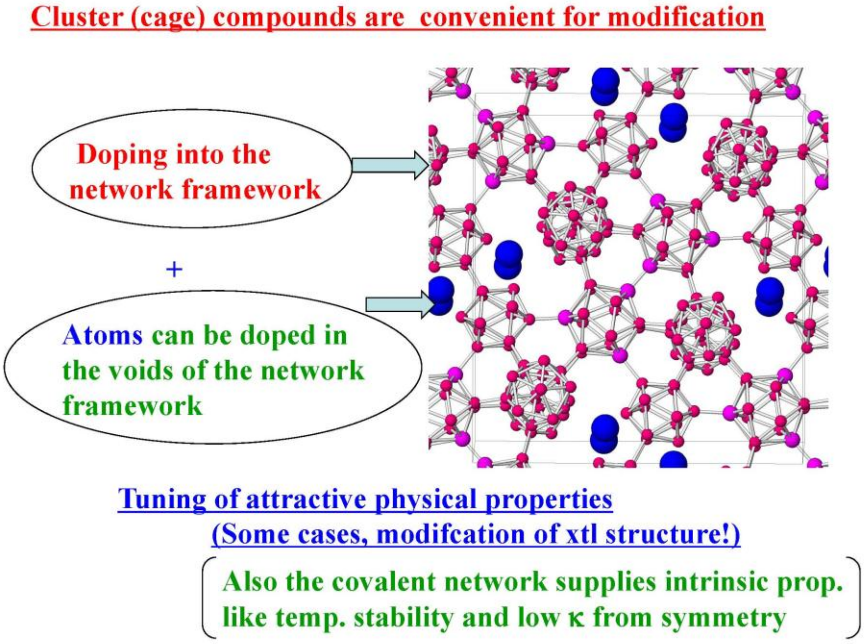

Fig. 3: Advantages of network structure

In the case of boron carbide, large enhancement of properties was obtained through network atom (B/C) substitution. The long awaited potential n-type counterpart to p-type boron carbide has structural similarities to boron carbide.

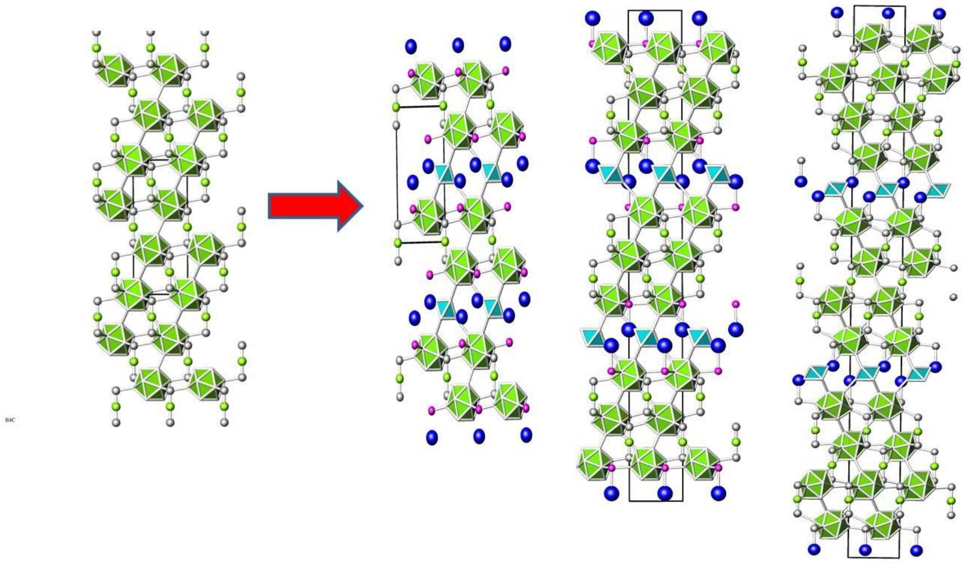

Fig. 4: View of crystal structure of boron carbide (left) and n-type counterparts (right)

Investigation of the network (framework) atom B/C exchange was carried out for $YB_{22}C_2N$. Structural properties have been studied from Rietveld refinement of the X-ray powder diffraction data for the series of $Y_{1-x}B_{22+y}C_{2-y}N$ samples revealing rather tiny homogeneity field for a certain range of Y concentration ($0.24 \leq x 0.30$ $11.5 \leq B/C \leq 12.7$). The small range of B/C for $Y_{1-x}B_{22+y}C_{2-y}N$ is a striking difference with boron carbide which exhibits a huge variation of $B_{12+x}C_{3-x}$ ($0.06 \leq x \leq 1.5$). Non-linear variation of lattice constants has been observed depending on the compositional change. The structure changes are accompanied by the site disorder at the chain-end carbon site. The contrasting values of displacement parameters for the icosahedron II boron sites may in general be indicative of the site disorder within this structural unit as well. With respect to thermoelectric properties, the smallest value of B/C ratio in the samples led to the best absolute values of Seebeck coefficient and the maximal power factor. This is a result somewhat matching intuition since the smaller B/C value equals an increase of carbon, namely electrons, in the n-type material. However, the range of B/C possible was indicated to be much smaller than boron carbide and is probably a result of the charge balance. In any case, although the adjustable range happens not to be large in this case, it is still demonstrated that the modification of the framework is a clear route for improvement of physical properties.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) papers published in peer-reviewed journals,

1) O. Sologub, Y. Matsushita and T. Mori, "α-Rhombohedral Boron Related Compound with Sulfur: Synthesis, Structure and Thermoelectric Properties", Scripta Materiala in press.
2) Y. Michiue, N. Kimizuka, Y. Kanke and T. Mori, "Structure of $(Ga_2O_3)_2(ZnO)_{13}$ and a unified description of the homologous series $(Ga_2O_3)_2(ZnO)_{2n+1}$", Acta Cryst. B68, 250–260, (2012).
3) T. Mori, I. Kuzmych-Ianchuk, K. Yubuta, T. Shishido, S. Okada, K. Kudou, and Y. Grin, Direct Elucidation of the Effect of Building Defects on the Physical Properties of alpha-$TmAlB_4$; an AlB_2-type analogous "tiling" compound", Journal of Applied Physics, 111, 07E127 (2012).
4) S. Okada, T. Shishido, K. Yubuta, and T. Mori, "Synthesis and some properties of a new chromium boride Cr_2B_3" Pacific Science Review, 14 (2011) 97-102.
5) W. Wunderlich, T. Mori, O. Sologub, and B. Baufeld, SPS-Sintering of $NaTaO_3$-Fe_2O_3 Composites, J. Austr. Cer. Soc. 47, 57-60 (2011).
6) Y. Michiue, T. Mori, A. Prytuliak, Y. Matsushita, M. Tanaka, and N. Kimizuka, "Electrical, optical, and thermoelectric properties of $Ga_2O_3(ZnO)_9$", RSC Advances, **1**, 1788-1793 (2011).
7) D. Berthebaud, A. Sato, Y. Michiue, T. Mori, A. Nomura, T. Shishido, and K. Nakajima, "Effect of transition element doping on crystal structure of rare earth borosilicides $REB_{44}Si_2$", Journal of

Solid State Chemistry, 184, 1682-1687 (2011).

8) T. Mori, K. Kudou, T. Shishido, and S. Okada, “f-electron dependence of the physical properties of $REAlB_4$; an AlB_2-type analogous “tiling” compound”, Journal of Applied Physics, **109**, 07E111 (2011).
9) J. Xu, T. Mori, Y. Bando, D. Golberg, D. Berthebaud, and A. Prytuliak, “Synthesis of CeB_6 thin films by physical vapor deposition and their field emission investigations”, Materials Science and Engineering B, 177, 117-120 (2011).
10) S. Okada, K. Kudou, T. Shishido, K. Yubuta, and T. Mori, “Synthesis And Physical Properties of $(Na_xRE_{1-x})AlB_{14}$ (RE=Li, Mg, Rare earths) Obtained By Molten Al Flux”, Solid State Phenomena, 170, 150-153 (2011).
11) D. Berthebaud, A. Sato, and T. Mori, “Nickel bismuth boride, $Ni_{23-x}Bi_xB_6$ [x = 2.44 (1)]”, Acta Cryst. **E67**, i17 (2011).
12) J. V. Zaikina, T. Mori, K. Kovnir, D. Teschner, A. Senyshyn, U. Schwarz, Y. Grin, and A. V. Shevelkov “Bulk and surface structure and high temperature thermoelectric properties of inverse clathrate-III in the Si–P–Te system”, Chemistry; a European Journal, 16, 12582-12589 (2010).
13) D. Berthebaud, T. Nishimura, and T. Mori, “Microstructure and thermoelectric properties of $YB_{22}C_2N$ dense samples fabricated through spark plasma sintering”, Journal of Electronic Materials, 40, 682-686 (2011).
14) A. Prytuliak and T. Mori, “Effect of transition metal additives on thermoelectric properties of $YB_{22}C_2N$”, Journal of Electronic Materials, 40, 920-925 (2011).

b) papers published in peer-reviewed conference proceedings,

c) papers published in non-peer-reviewed journals and conference proceedings,

1. T. Mori, "Rare earth borides, carbides, and nitrides", in: *The Rare Earth Elements: Fundamentals and Application*, ed. D. Atwood (J. Wiley & Sons, Chichester), in press (2012).
2. T. Mori, “Boride Thermoelectrics; High temperature thermoelectric materials”, in: *Modules, Systems and Applications*, ed. D. M. Rowe, (Taylor and Francis, London), in press (2012).
3. 森孝雄
“ホウ素系高温熱電変換材料”「熱電変換技術—クリーンエネルギーをめざして—」シー・エム・シー出版, (2011) 72-83. (in Japanese)
4. T. Mori, “High Temperature Boron-based Thermoelectric Materials”, in: *Thermoelectric Conversion Technology – The Search for Clean Energy*, ed. T. Kajikawa, (CMC, Tokyo, 2011) 72-83.
5. T. Mori, "Magnetic and Thermoelectric Properties of Boron-Rich Solids", in: *Boron Rich Solids, Sensors, Ultra High Temperature Ceramics, Thermoelectrics, Armor*, ed. N. Orlovskaya and M. Lugovy (Springer, New York), pp. 63-82 (2010).

d) conference presentations without papers,
Listing only Invited Talks to large international conferences

1. Takao Mori, MRS Spring Meeting 2012, “Nanostructured Borides and Perspectives of High Temperature Thermoelectric Materials”, San Francisco, USA, April 9~13, 2012.
2. Takao Mori, ISBB2011 (17th International Symposium on Boron, Borides and Related Materials), “Origin of Low Thermal Conductivity in Boride Compounds”, Istanbul, September 15th, 2011.
3. Takao Mori, Troisieme Cycle Seminar; Workshop on Synthesis and Function of Thermoelectric Materials, “Finding Novel Routes to Intrinsically Lower Thermal Conductivity”, Villars, Switzerland, Aug. 16th, 2011.
4. Takao Mori, MRS Fall Meeting 2010, “Advances in Thermoelectric Perspective of Borides”, Boston, USA, November 29th, 2010.

e) manuscripts submitted but not yet published, and

1. O. Sologub, Y. Michiue and T. Mori, “Structural and thermoelectric properties of $Y_{1-x}B_{22+y}C_{2-y}N$”, submitted to Journal of Physics and Chemistry of Solids.
2. N. Tsujii and T. Mori, “High Thermoelectric Power Factor in a Carrier-Doped Magnetic Semiconductor $CuFeS_2$”, submitted to Applied Physics Letters.
3. M. A. Kirsanova, T. Mori, M. Matveeva, D. Batuk, A. M. Abakumov, A. V. Gerasimenko, A. V. Olenev, Y. Grin, A. V. Shevelkov, “Synthesis, crystal and electronic structure, and transport

properties of type-I semiclathrates $Ge_{46-x}P_xSe_{8-y}$ ($x \approx 15.4$; $y = 0$–2.65)", submitted to Inorganic Chemistry.

4. A. Prytuliak, S.Maruyama, and T. Mori, "Anomalous effect of vanadium boride seeding on thermoelectric properties of $YB_{22}C_2N$", submitted to Materials Research Bulletin.

f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

Attachments: Publications a), b) and c) listed above if possible.

DD882: As a separate document, please complete and sign the inventions disclosure form.

Important Note: If the work has been adequately described in refereed publications, submit an abstract as described above and refer the reader to your above List of Publications for details. If a full report needs to be written, then submission of a final report that is very similar to a full length journal article will be sufficient in most cases. This document may be as long or as short as needed to give a fair account of the work performed during the period of performance. There will be variations depending on the scope of the work. As such, there is no length or formatting constraints for the final report. Keep in mind the amount of funding you received relative to the amount of effort you put into the report. For example, do not submit a $300k report for $50k worth of funding; likewise, do not submit a $50k report for $300k worth of funding. Include as many charts and figures as required to explain the work.